Aerosol source apportionment from 1-year-measurements at the CESAR tower at Cabauw, NL

P. Schlag[1,2], A. Kiendler-Scharr [2], M. J. Blom[3], F. Canonaco[4], J. S. Henzing[5], M. Moerman[5], A. S. H. Prévôt[4] and R. Holzinger [1]

[1]Institute for Marine and Atmospheric Research Utrecht (IMAU), Utrecht University, Utrecht, The Netherlands

[2]Institute for Energy and Climate Research (IEK-8): Troposphere, Forschungszentrum Jülich, Jülich, D-52425, Germany

[3]Energy Research Centre of the Netherlands (ECN), Petten, The Netherlands

[4]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), Villigen, Switzerland

[5]Netherlands Organisation for Applied Scientific Research (TNO), Utrecht, The Netherlands

Correspondence to: P. Schlag (p.schlag@fz-juelich.de)

Responses to anonymous referee #4

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We thank the reviewer for the careful review of our manuscript; the comments and suggestions are greatly appreciated. All the comments have been addressed. In the following please find our responses to the comments one by one and the corresponding changes made to the manuscript. The original comments are shown in italics.

Specific Comments:

1) P35123, L27: Contrary to what is implied, the Middlebrook parameterisation does take account of the nitrate mass fraction. More justification should be given in the main article on why it was not suitable here because it would be preferable to use the SMPS data for an independent validation, rather than informing the CE.

Response:

The SMPS was sampling from the inlet located at 60 m height while the ACSM sampled from the roof at 5 m height, resulting in a higher uncertainty comparing to the usual set-up where both instruments would sampling from inlets close together. In addition and as responded to the similar comment from referee #1, the application of the Middlebrook algorithm lead to unreasonable discontinuities of CE value. The algorithm used in the work originated from the comparison of a ToF-AMS with the same SMPS, both sampling from the 60 m-inlet, during a campaign in Cabauw in May 2008 (Mensah et al., 2012). But the authors agree that the current explanation is misleading. In the revised manuscript the respective part was changed to:

"In contrast to the commonly used constant value of 0.5 this CE correction accounts for the high ammonium nitrate mass fraction (ANMF) found at this site and is thus more suitable for the data presented here. Another algorithm for composition dependent CE determination (Middlebrook et al., 2012) was also tested for its validity. It uses a threshold ratio of measured to predicted NH_4 to switch between two different equations to determine the CE. The threshold value of 0.75 is close to the observed ratio of measured over predicted NH4 of this data set, resulting in large discontinuities of CE values and in consequence, discontinuous changes in aerosol mass concentrations. In other words, the Middlebrook algorithm is not

suitable for data sets showing at the same time low ratios of measured to predicted NH_4 and high AMNF's."

2) P34124, L25: Was the factory default inversion and calibration of the MAAP used? If so, this should be specified.

Response:

Indeed, the factory default inversion and calibration was used to determine the eBC concentrations from MAAP data. We agree that this information should be added in the revised manuscript. In addition to other changes due to comments from other referees, the MAAP description was changed as follows:

"The MAAP instrument has been introduced by Petzold and Schönlinner (2004) and Petzold et al. (2005). It is designed for the determination of the black carbon (BC), which is a product of incomplete combustion. There is in the scientific community a general consensus over what black carbon is in terms of properties (Bond et al., 2013) The MAAP measures the strong visible light absorption property of BC by simultaneous measurements of the radiation penetrating through and scattered back from a particle-loaded fiber filter. According to Petzold et al. (2013), optical BC determined by MAAP is to be referred to as equivalent black carbon (eBC). One property of BC is that it is highly refractory with a vaporization temperature near 4000K (Schwarz et al., 2006), thus BC is not vaporized at 600°C and cannot be measured by the ACSM. The MAAP achieves a time resolution of 5 minutes with an uncertainty of 12% (Petzold and Schönlinner, 2004). The eBC mass concentration was determined using the factory default inversion and calibration."

3) P35125, L3: The model numbers of the SPMS and CPC should be given.

Response:

The SMPS used in this work is actually a combination of a DMA and a CPC in one instrument. We agree that the model number of this instrument should be given. In the revised manuscript, this part was therefore changed to:

"The SMPS (TSI, Model 3034) is a sequential combination of several integrated components: an impactor, a neutralizer, a differential mobility analyzer and a condensation particle counter. It determines the size distribution of particles in a range of 10 nm to 487 nm (electro-mobility diameter)."

4) P35125, L23: More detail should be given regarding how the losses down the inlet pipe were calculated, given the magnitude of the correction. In particular, if diffusional losses were significant, whether this correction should be size-dependent should be commented on.

Response:

As responded to a similar comment from referee #1, we used now the particle density deriving from the chemical composition not as the campaign average but time resolved for each data point in the revised manuscript. In addition we introduced SMPS data which is now size dependently corrected as published by Henzing (2011) The description of the sampling losses of the 60 m inlet for eBC given in the manuscript derived from a series of measurements at the Cabauw tower performed in a previous campaign. Unfortunately these results are not published yet. To clarify how these losses were determined in the revised manuscript and to account for a comment from referee #2, the loss description was changed as follows:

"SMPS data was corrected size dependently for (diffusional) losses in the inlet system and SMPS system itself according to (Henzing, 2011) who compared theoretical findings with measured losses that are obtained by measuring simultaneously before and after the various parts of the inlet system at the CESAR tower. In addition, particles of different compositions were measured in 2013 simultaneously at the pipe entrance at 60 m height and in the basement (J. S. Henzing, personal communication). For more than 8000 simultaneous observations, the results showed that aerosol measurements through this 60 m sampling line underestimate PM_{10}-eBC by approximately 33% with an uncertainty of 7%. Therefore, eBC obtained from the MAAP are divided by a factor of 0.66 to account for these losses. For the inorganic species penetrations through this inlet line were reported to be 62-73% for nitrate, 55-64% for sulfate, and 54-56% for ammonium. However these results were not used for corrections in this work"

Please note that these losses influenced only data acquired by the MAAP and SMPS. Since the contribution of eBC is rather low (average: 5%) a potential overall error for total aerosol masses is low and would not significantly alter one quintessence of the paper, namely total mass concentrations above the air quality limits. We think theoretical particle loss calculations would not add additional information in the context of this paper.

As a consequence of the newly evaluated SMPS data the correlation values between ACSM+MAAP data with SMPS data changed as seen in Fig. S3 and S4 in the revised supplement. Nevertheless, the overall qualitative and quantitative agreement is still given

except that the ACSM+MAAP data is now overestimating the total PM_1 mass by 16%, excluding the eBC data the ACSM overestimates total mass by 12%. As seen in Fig. S3 the difference between both systems is significantly higher during the pollution events 16 to 27 January 2013 and 5 to 8 May 2013. Since the quantitative agreement with the MARGA is much higher at these times the discrepancy to the SMPS is likely due to the fact that the losses within the 60 m inlet could not be corrected for individual species as mentioned above. Therefore the following paragraph was added at the end of the cross validation chapter in the revised manuscript:

"Major discrepancies to the SMPS especially during some of the pollution events like 16 to 27 January 2013 and 5 to 8 May 2013 (see below) can be explained by the correction of losses through the 60 m inlet line which was done size dependently and did not account for losses of individual species as mentioned in chapter 2.3. As the quantitative agreements of individual inorganic species as well as of total inorganics between the ACSM and the MARGA during these periods are much higher, the mass loadings determined from these instruments are more reliable than the SMPS data."

5) P35126, L13: Polyethylene is not a conductive polymer, so electrostatic losses of particles should be expected. Has this inlet line been characterised for this?

Response:

As responded to the similar comment from referee #1 a polyethylene (PE) tube can indeed potentially enhance wall losses of particles comparing to stainless steel tubes. The MARGA-inlet system at the Cabauw tower as used for this study was previously described by Schaap et al. (2011). It actually did not only consist of PE tubes but of a series of components reducing particle losses. They investigated wall losses on a similar system and found only minor concentration losses for several compounds of 2% and less. A more detailed description was added in the revised manuscript:

"The sample air was transferred into the instrument within a polyethylene („Polyflo") tube with an inner diameter of 0.5" (= 1.27 cm) and a sample flow of 16.7 L min^{-1}, which is either directed through a PM_1 or a $PM_{2.5}$ size selective head. A detailed description of the MARGA inlet system at the Cabauw tower was previously described by Schaap et al. (2011). There, wall losses were investigated and found to be less than 2% for several gaseous and particulate compounds."

6) P35126, L15: The method of size selection (e.g. impaction, cyclone) should be specified.

Response:

The size selection was done using size selective cyclones. We agree that this should be specified. This part was changed in the revised manuscript to:

"The sample air was transferred into the instrument within a polyethylene („Polyflo") tube with an inner diameter of 0.5" (= 1.27 cm) and a sample flow of 16.7 L min^{-1}, which is either directed through a PM_1 or a $PM_{2.5}$ size selective cyclone."

7) P35133, L3: I don't see how the sulphate comparison can be regarded as "high quantitative agreement" given that it is of the order of 50% out. Given that historically, comparisons regarding sulphate generally tend to be quite favourable, this is quite surprising. It is also a little worrying that the ACSM measures more than both the AMS and the MARGA. The authors should investigate this further.

Response:

The "very high qualitative and quantitative agreements" is just referring to the comparison of the total inorganic masses from both instruments as shown in the last plot of Fig. S11 (which changed to Fig. S5 in the revised supplement). The authors agree that the current description is misleading because the word "agreements" is written in the plural form. In the revised manuscript, this word was changed to its singular form "agreement".

As seen by the last plots in Fig. S11 and S12 (which changed to Fig. S5 and S6, respectively, in the revised supplement), the ACSM actually measures the same or even little less than the MARGA and AMS, respectively, in terms of total concentrations (slopes of the regression lines are 1.05 and 0.90, respectively). The ACSM showed higher concentrations only in case of nitrate. This issue and the discrepancies regarding other aerosol species is explained in detail in the manuscript and in the responds to similar comments from referees #1 and #2.

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